



Experiment title: Domain Orientation and Orientation Kinetics of Block Copolymer Solutions under the Influence of Electric Fields

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Report:

The present project tries to establish a microscopic understanding of the processes involved in electric field induced micro domain alignment in phase separated block copolymers solutions. The microscopic state of order is followed in-situ during the alignment process by synchrotron SAXS. In order to investigate the influence of the electric field strength on the orientation kinetics we varied the electric field between 0.25 kV/mm and 3 kV/mm. A 35 wt.-% solution of $S_{50}I_{50}^{80}$ was studied at room temperature¹. A selection of P_2 curves is shown in Figure 1. In addition, we investigated the electric field dependent orientation behavior of a 40 wt.-% solution of $S_{50}V_{50}^{78}$ and a 40 wt.-% solution of $S_{43}H_{10}M_{47}^{82}$.

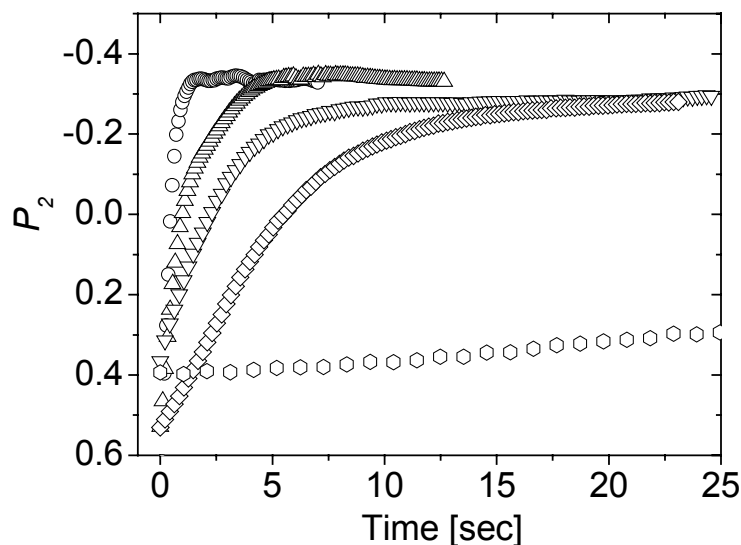


Figure 1: Evolution of orientational order parameter P_2 with time for 35 wt.-% solutions of $S_{50}I_{50}^{80}$ at different field strengths ($\circ = 375$ V/mm, $\diamond = 1$ kV/mm, $\nabla = 1.25$ kV/mm, $\triangle = 1.5$ kV/mm, $\square = 3$ kV/mm, electrode spacing: 2 mm).

In the case of the PS-*b*-PI system for example, the time constants τ range from 100 sec for low electric fields (0.375 kV/mm) to as low as 0.34 sec for the highest field strength (3 kV/mm). On the time scale of our experiment, we were not able to detect any reorientation for electric fields below 0.375 kV/mm. We may therefore conclude that there exists a threshold field strength E_t between 0.25 kV/mm and 0.375 kV/mm, below which no field induced reorientation is possible. Above E_t , the dependence of the time constant on the electric field reveals a power law dependence $\tau = \alpha(E - E_t)^a + \tau_\infty$. The data points are best fitted for $\alpha = 0.2 \text{ sec } a = -1$, $E_t = 350 \text{ V/mm}$ and $\tau_\infty = 0 \text{ sec}$ (solid line in Figure 2A).

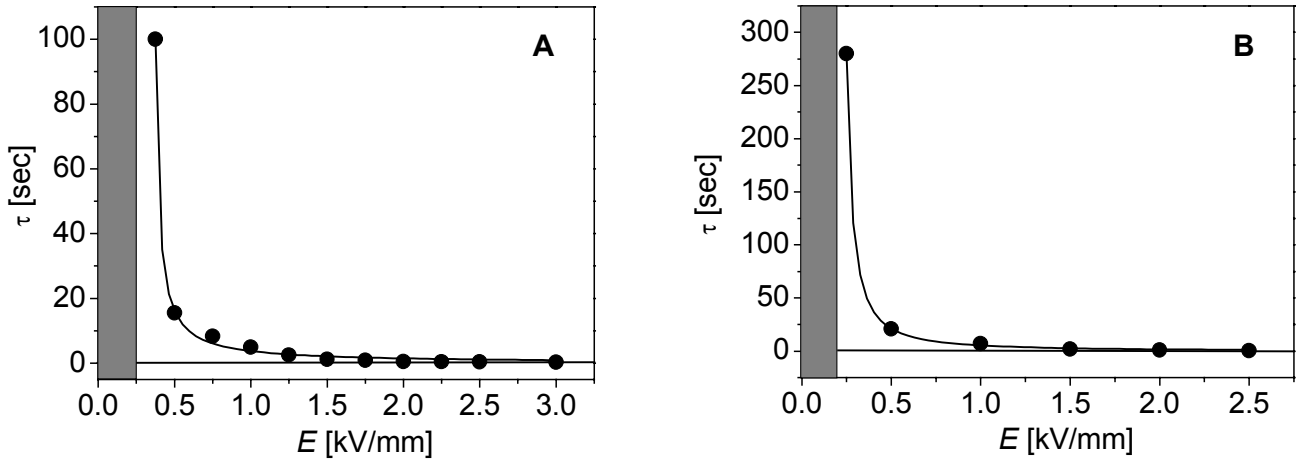


Figure 2: Electric field dependence of time constant τ for a 35 wt.-% solution of $S_{50}I_{50}^{80}$ (A) and a 40 wt.-% solution of $S_{50}V_{50}^{78}$ (B) (electrode spacing: 2 mm). The solid line represents a least-squares fit to the power law $\tau = \alpha(E - E_t)^a + \tau_\infty$ to the data points with $E_t = 350 \text{ V/mm}$ and $E_t = 200 \text{ V/mm}$, respectively.

The dependence of the time constant τ on the electric field strength exhibits a hyperbolic power law as described above. The asymptotic behavior at high electric fields (i.e. for a large force acting on the lamellae) indicates $\tau_\infty = 0 \text{ sec}$ for infinite field strength. This is expected in the absence of any electrorheological effects and limits in single chain diffusion, as the dominating process at 35 wt.-% is the migration of grain boundaries. The asymptotic behavior at low field strength indicates a threshold value E_t of some 0.35 kV/mm. This is in agreement with the experimental observation that at lower field strengths no effect of the electric field on the scattering pattern was observed. This threshold value can be explained by a competition of the electric field and the surface field generated by the gold electrodes. The latter exhibits an unexpected range, as has already been found by Annighöfer and Gronski for thick PS-*b*-PI block copolymer bulk samples cast from several aromatic solvents (including toluene) in the absence of an external electric field². We always find 10 to 40 lamellar layers parallel to the boundary electrodes with a transition to lamellae perpendicular to the electrodes, as reported earlier³. As the formation of T-junctions for the transition from lamellae parallel to perpendicular to the boundary surfaces leads to an energetic penalty which has to be balanced by the electric field, we can define the threshold field strength as the voltage needed to overcome this energetic barrier. Therefore, a sufficient gain in energy is required, which can be derived from the overall size of the domains to be aligned parallel to the electric field vector.

Polymer	E_t [kV/mm]	$\Delta\epsilon$
PS- <i>b</i> -PI	350	0.2
PS- <i>b</i> -PHEMA- <i>b</i> -PMMA	310	2.2
PS- <i>b</i> -P2VP	200	5.1

Table 1: Threshold field strengths and dielectric contrast of different diblock copolymers.

Another property common to all diblock copolymer samples is the low threshold field strength which ranges between 200 and 350 V/mm and decreases with increasing polarity of the second block. In the sequence PS-*b*-PI/PS-*b*-PHEMA-*b*-PMMA/PS-*b*-P2VP, the asymmetry in the surface tension between the blocks increases and therefore the interaction with the electrode surface field becomes stronger, i.e. one of the blocks interacts with the surface increasingly stronger than the other block and the surface field strength increases. In a recent theoretical work, Tsori and Andelman⁴ have predicted that the threshold field strength for a transition from an alignment of the lamellae parallel to the electrodes to a mixed morphology (formation of T-junctions) only depends on the dielectric contrast between the blocks, i.e. a larger dielectric contrast is expected to decrease the threshold field. This prediction is corroborated by our experimental results as the threshold field strength for our systems decreases with increasing dielectric contrast as shown in Table 1. This agreement is even more surprising as intuitively one would have expected the polarity of the second block of our systems to lead to an increase in the threshold field strength due to a stronger surface field.

A more detailed description of this work will be published elsewhere⁵.

References

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- ³ Böker, A.; Knoll, A.; Elbs, H.; Abetz, V.; Müller, A.H.E.; Krausch, G. *Macromolecules* **2002**, *35*, 1319.
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